

## KEROGEN CONSTITUENTS: REDUCED CHLOROPHYLLIN AS A MODEL FOR THE PRECURSORS OF NITROGENOUS COMPOUNDS IN SHALE OIL

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### INTRODUCTION

In evaluating and developing the resource potential of the Nation's vast oil-shale reserves, the U.S. Bureau of Mines has been conducting research in the origins and chemistry of shale oil. As part of this work, the role of plant pigments and their decomposition products as possible precursors of the nitrogenous compounds found in shale oil was investigated. An accurate picture of the origin of the compounds and their compound types may be an aid in analyzing the character of the oil, its suitability as a refinery feedstock, or perhaps its importance as a source of commercially valuable chemical compounds.

The idea that plant pigments may be the origin of nitrogen-containing compounds in shale oil is not new. Mapstone has proposed that the pyrroles found in shale oil result from the pyrolysis of the porphyrins in chlorophyll.<sup>1</sup> It has been shown that kerogen, the organic phase of oil shale, is 45 to 60 percent heterocyclic material.<sup>2</sup> This work was undertaken to substantiate Mapstone's proposal and to see if plant pigments could be the origin of the heterocyclic material in kerogen.

Experimentally, a comparison between the nitrogen compounds in a shale-oil light distillate and the nitrogenous compounds found in the pyrolysates of chlorophyll derivatives was made. The similarity of the compounds found in both the shale oil and chlorophyllin pyrolysate indicates that reduced chlorophyllin derivatives are a good model for the portion of kerogen that produces nitrogen compounds upon pyrolysis of oil shale. The present paper describes the preparation and characteristics of the kerogen model and shows that pyrolysis of this model yields pyrroles and products which are comparable to the nitrogenous products of shale oil.

### EXPERIMENTAL PROCEDURE

#### Description of Materials

##### Commercial Chlorophyllin

Chlorophyllin is commercially available as the trisodium-copper salt with the empirical formula  $C_{31}H_{31}N_4Cu(CO_2Na)_3$ . Most processes for commercial production of chlorophyllin involve saponification of plant material, and the resulting product frequently contains fatty acid salts as impurities.<sup>3</sup> A commercial sample of chlorophyllin with a nitrogen content of 4.83 percent was used in this study. This compares with the theoretical value of 7.73 for the pure salt, indicating that the commercial sample is 63 percent pure. The remaining material is assumed to be fatty acid salts.

##### Shale-Oil Light Distillate

Samples for mass spectral analysis were obtained as follows. A 110-g sample of an in situ shale-oil light distillate was separated on 880 g of Florisil. Each fraction was monitored by infrared spectroscopy as a 2-percent solution in carbon tetrachloride. The fraction richest in pyrrolic

N-H (as indicated by the intense band at  $3,480\text{ cm}^{-1}$ ) was further fractionated into six subfractions, A<sub>0</sub>-A<sub>5</sub>, using the method of Snyder and Buell for separations on alumina.<sup>4</sup> Three of the subfractions--A<sub>2</sub>, A<sub>3</sub>, and A<sub>5</sub>--were sufficiently different in the IR to be examined individually by mass spectroscopy, along with two later fractions which gave indications in the infrared of meriting further study.

### Reduction and Pyrolysis of Chlorophyllin

#### Reduction

The reduction of chlorophyllin with PtO<sub>2</sub> in glacial acetic acid with the resultant uptake of three moles of hydrogen to give hexahydrochlorophyllin is reported in the literature<sup>5</sup> as a straightforward reaction, but this was not found to be so during the course of this study. Using a PtO<sub>2</sub>-to-chlorophyllin ratio of 2:25, H<sub>2</sub> pressure of 275 psig (at 25° C), and heating to 150° C for 72 hours resulted in only partial reduction. At no time during this study was the success of the reaction predictable. In each case the reduced platinum was removed by filtration, and the acetic acid was removed with mild heat and vacuum on a rotary evaporator. The resulting dark brown material was the synthetic kerogen which was pyrolyzed to yield the oils which were compared with shale oil. For additional comparison, a sample of commercial chlorophyllin was dissolved in acetic acid and then recovered by the above technique to yield chlorophyllin acetate for pyrolysis.

#### Pyrolysis of Reduced Chlorophyllin

Samples to be pyrolyzed (~10 g) were placed in a 300-ml flask which was connected to a trap cooled with liquid nitrogen. The system was evacuated to  $\sim 10^{-2}$  mm for at least 30 minutes; then the pressure was reduced to  $\sim 10^{-5}$  mm, and heat was applied to the sample container with a hot air bath. Heat was applied slowly, and as it approached 200° C a clear distillate began to collect in the trap. This was believed to be excess acetic acid and perhaps some water. The pressure in the system also took a rapid jump to  $\sim 10^{-2}$  mm Hg as CO<sub>2</sub> was eliminated from the acids present. After the pressure began to drop, additional heat was applied until the temperature in the air bath reached 375° C to 425° C. The temperature was maintained at this level until no more distillate, a dark red-brown liquid, was observed coming from the sample. At this point the pressure had risen to  $10^{-2}$  mm Hg and remained fairly constant. The heating was discontinued, the system was allowed to cool to room temperature, and the pressure was returned to normal. The frozen distillate was dissolved in ethyl ether and washed with saturated NaHCO<sub>3</sub> until the wash water was basic. The sample was dried over anhydrous K<sub>2</sub>CO<sub>3</sub>, and the ether was removed at room temperature under a slight negative pressure. If the acetic acid and water were not removed immediately, the sample tended to polymerize and form heavy precipitates. The samples were stored under a nitrogen atmosphere at 0° C.

### Characterization Procedures

#### Chromatographic Separation and Analysis

The pyrolysates from chlorophyllin and a reduced chlorophyllin were treated with an ion-exchange resin to separate the basic from the neutral material in the following manner. Two ml of a 5-percent solution of the pyrolysate in cyclohexane were passed through a column containing 1.0 g of activated Rohm and Haas Amberlyst 15 cation-exchange resin with cyclohexane as the solvent. The first 2 ml of eluent were collected and used in the subsequent analysis. GC analysis by simulated distillation of aliquots of the solution before and after treatment and comparison of the sample areas gave percent basic nitrogen in the total sample. Breakdown of the GC output in terms of 50° C increments gives the relative distribution of compounds according to boiling range and, by inference, according to molecular weight.

### Titrimetric Analysis

Titration of the bases in the pyrolysates was done in acetic anhydride and in acetonitrile using an autotitrator. The titrations were performed on samples containing about 0.1 milliequivalent of nitrogen, using 0.1 N perchloric acid in dioxane based on the methods of Wimer<sup>6</sup> and Buell.<sup>7</sup> The electrode system was glass versus calomel reference, and the electrolyte in the calomel electrode was methanolic KCl.

### Infrared Analysis

Qualitative spectra of all fractions were run as 2-percent solutions in carbon tetrachloride with 0.5-mm NaCl cells. Quantitative pyrrolic N-H was determined by the method of Koros, et al.<sup>8</sup>

### Mass Spectral Analysis

Low-ionizing voltage mass spectrometry at 14 to 16 nominal volts was used to obtain the molecular weights of the various homologous series in various samples. High-resolution spectra were run at 70 eV to confirm the empirical formulas of the various ions.

## RESULTS AND DISCUSSION

Table 1 lists the elemental composition of the starting materials as well as the distillates

TABLE 1. - Elemental composition of the starting materials, distillates, and residues from the pyrolysis of some samples of chlorophyllin and its related products

Sample	Carbon, wt-pct	Hydrogen, wt-pct	Nitrogen, wt-pct	Carbon/hydrogen
Chlorophyllin	59.46	5.82	4.83	0.85
Distillate	85.31	9.31	5.18	.76
Residue	59.50	4.16	5.41	
Chlorophyllin acetate	58.45	6.14	4.26	.79
Distillate	85.31	9.78	4.49	.73
Residue	59.67	4.08	5.29	
Reduced chlorophyllin A <sup>1</sup>	60.07	6.53	2.88	.77
Distillate	85.21	10.90	2.96	.65
Residue	59.49	3.82	5.04	
Reduced chlorophyllin B <sup>1</sup>	46.24	6.03	2.19	.64
Distillate	80.85	10.00	4.78	.67
Residue	38.45	2.73	2.99	

<sup>1</sup> Reduced chlorophyllin A and B are products of two separate reductions of commercial chlorophyllin with PtO<sub>2</sub>.

and residues from the pyrolysis of some samples of chlorophyllin and related products. The reduction caused some hydrodenitritification, as shown by the lowered nitrogen percentages. Upon pyrolysis, the two reduced materials gave the products with the lowest carbon-hydrogen ratio as would be expected.

Figure 1 shows the distribution of basic and neutral compounds as defined by their affinity for adsorption on Amberlyst 15 resin. Pyrolysis of reduced chlorophyllin produces 50 percent more basic material than does pyrolysis of the nonreduced material, and it is noteworthy that most of this additional material is fairly low boiling, falling in the 200 to 300° C range.

Titration of the pyrolysates in nonaqueous solvents gives information concerning the strength of the various bases present. These data are presented in table 2. There appears to be no correla-

TABLE 2. - Nitrogen composition of distillates

Distillate source	Titrateable N, total	Wt-pct strongly basic	Wt-pct weakly basic	Wt-pct very weakly basic
Chlorophyllin	1.52	0	0.78	0.74
Chlorophyllin acetate	1.68	0	1.22	.46
Reduced sample A	1.57	0	.76	.81
Reduced sample B	3.08	0	.82	2.25

tion between the amount of hydrogen in the starting material and the types of bases formed, but the presence of bound acetic acid does favor the production of weak bases at the expense of the very weak bases.

Tables 3 and 4 list the homologous series of nitrogen compounds found in the low-ionizing-voltage mass spectrum of the reduced chlorophyllin pyrolysate having the highest pyrrolic N-H content, 2.02 percent, and the five fractions of the shale-oil light distillate, respectively. High-resolution mass spectra on reduced chlorophyllin pyrolysates confirm the presence of all the mononitrogen series of compounds listed in table 3. In the shale-oil light distillate, the  $Z = -3$  series is missing from the high-resolution mass spectrum. Its absence is unusual because pyrroles have been isolated from shale oil.<sup>9</sup> The absence of the  $Z = +1$  series in the mass spectrum of the pyrolysate is not too surprising; few materials in such a reduced state would be expected from the thermal decomposition of what is basically a hydrogen-poor substrate. The absence of the  $Z = -7$  series in the reduced chlorophyllin pyrolysate cannot be explained at this time, but it has been found in other reduced chlorophyllin pyrolysates.

For the  $Z$  series (-3, -5, -7, -11) found in various chlorophyllin pyrolysates by mass spectrometry, the following compound types are probably represented: Pyrroles (-3); cycloalkylpyrroles, pyridines (-5); cycloalkylpyridines (-7); indoles (-9); and azanaphthalene derivatives (-11). These represent materials whose presence has been reported in shale oil before<sup>9,10</sup> or that were found in this work. It is felt, therefore, that chlorophyllin derivatives, especially the reduced materials, represent a reasonable model for the portion of kerogen that produces nitrogen-containing compounds upon pyrolysis.

#### SUMMARY

The reduction and pyrolysis of a commercially available plant pigment extract, chlorophyllin, is described. The amounts of bases formed and their boiling-range distribution are related to the hydrogen content of the starting materials. Mass spectral studies are given which show that many of the same types of bases are found in the pyrolysate and in an in situ light distillate. These results indicate that reduced chlorophyllin may be used as a model for the nitrogen-containing constituents in kerogen.

TABLE 3. - Mononitrogen-containing molecular ions in the low-ionizing voltage mass spectrum of reduced chlorophyllin pyrolysate

Series	General formula	Carbon No. range	Rings plus double bonds
I-a	$C_nH_{2n-3}N$	6-14	3
I-b	$C_nH_{2n-5}N$	7-15	4
I-c	$C_nH_{2n-9}N$	10-15	6
I-d	$C_nH_{2n-11}N$	14-18	7

TABLE 4. - Nonnitrogen-containing molecular ions from the low-ionizing voltage mass spectra of chromatographic fractions of shale-oil light distillate

Series	General formula	Carbon No. range	Rings plus double bonds
<u>Fraction A<sub>2</sub></u>			
II-a	$C_nH_{2n+1}N$	8-14	1
II-b	$C_nH_{2n-11}N$	10-13	7
II-c	$C_nH_{2n-9}N$	10-14	6
<u>Fraction A<sub>3</sub></u>			
II-d	$C_nH_{2n-11}N$	9-14	7
<u>Fraction A<sub>5</sub></u>			
II-f	$C_nH_{2n-7}N$	8-12	5
II-g	$C_nH_{2n-9}N$	12-15	7
<u>Fraction 42</u>			
II-h	$C_nH_{2n-9}N$	8-12	6
II-i	$C_nH_{2n-11}N$	11-15	7
II-j	$C_nH_{2n-13}N$	13-15	8
<u>Fraction 58</u>			
II-k	$C_nH_{2n-5}N$	8-15	4
II-l	$C_nH_{2n-11}N$	9-14	7

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Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

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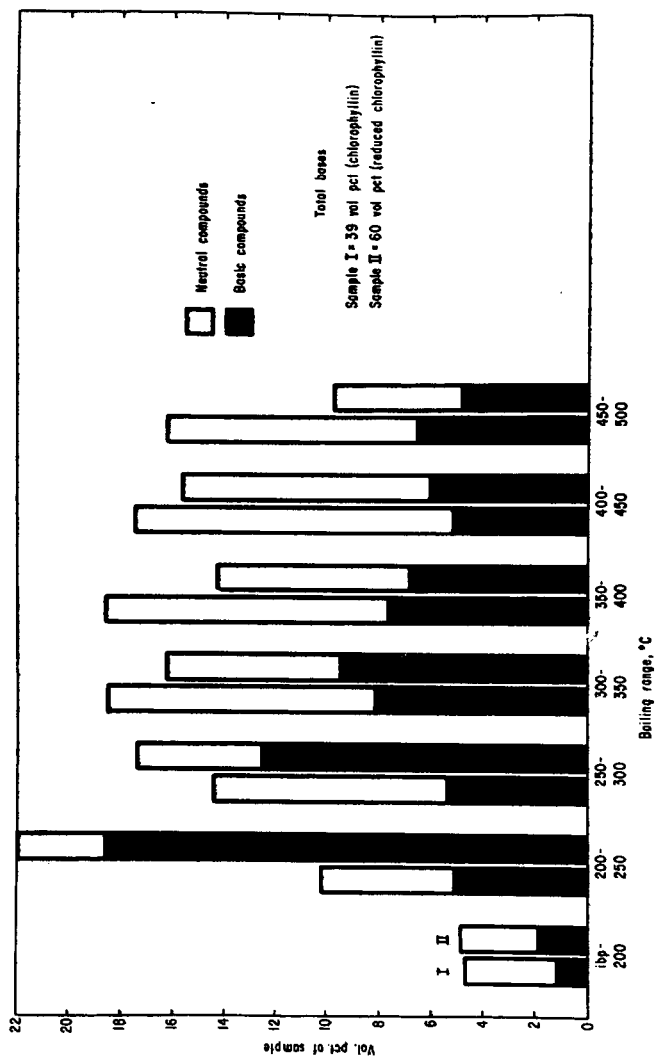


FIGURE 1. - Distribution of compounds in distillates.